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Treatment of Seasonal Pesticides in Surface Waters

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TREATMENT OF SEASONAL PESTICIDES IN SURFACE WATERS

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ABSTRACT

Numerous pesticides were monitored in surface waters in agricultural areas. Atrazine, alachlor, metolachlor, cyanazine, metribuzin, carbofuran, linuron, and simazine were found in the influent to three water treatment plants in storm runoff following their application. Studies at these plants, together with bench-scale studies, demonstrated poor control by conventional treatment processes. The relatively high adsorption capacities of these agrichemicals indicate that GAC can be cost-effective for their control. PAC applied at taste-and-odor control doses can also be effective if moderate percent removal is required.

In the 1986 Amendments to the Safe Drinking Water Act, the Congress required that maximum contaminant levels (MCLs) be promulgated for numerous, highly water-soluble pesticides within three years of enactment. Among them were alachlor, atrazine, simazine, and carbofuran. A National Pesticide Survey of groundwaters by the U.S. EPA will include these, as well as metolachlor, cyanazine, linuron, and metribuzin, among the many compounds it will monitor (1). The Water Quality Laboratory (WQL) at Heidelberg College has monitored these pesticides and a number of others in the tributaries of Lake Erie since 1982 as a part of their efforts to assess the impact of agricultural practices on the Great Lakes. These eight pesticides were detected in the tributaries as a result of runoff following their springtime application. Because several of the tributaries serve as raw water sources for municipal water treatment plants, the WQL, together with three northwest Ohio water treatment plants, joined in a cooperative effort with U.S. EPA's Drinking Water Research Division (DWRD) to examine the fate of these pesticides during treatment. The DWRD has further examined these pesticides on the bench-scale using spiked Ohio River water. These studies will serve as one of the first attempts to assess control of these pesticides, will aid in defining treatability before setting MCLs, and will assist impacted water utilities in selecting control processes.

Heidelberg College and its WQL are located in Tiffin, a community in northwestern Ohio. Approximately 78 percent of the land area in northwestern Ohio watersheds is used for row crop agriculture (2). Corn and soybeans are the principal crops. The WQL's program in Lake Erie tributary monitoring began in 1974 under a grant from the U.S. Army Corps of Engineers (3). Monitoring focused on sediments, phosphorus, and nitrogen compounds

that moved into the lake from agricultural watersheds. Studies indicated that conservation tillage could significantly reduce nutrient and sediment loading to the lake (4). Environmental concern that increased use of conservation tillage could increase pesticide contamination of surface water led the WQL to inititate pesticide monitoring programs in Lake Erie tributaries in 1982. Tables 1 and 2 summarize herbicide and insecticide use in Ohio in 1982 (5). Analytical methods were developed at the WQL to allow for quantitation of many of the pesticides listed in Tables 1 and 2 (6). WQL sampling took place at USGS stations on Lake Erie's tributaries. This allowed a coupling of the nutrient or pesticide data with streamflow data in order to assess lake loading. When studies of the fate of pesticides during water treatment became an objective, river water sampling was extended to plant intakes.

Three plants participated in the study. The Tiffin District of the Ohio-American Water Company and the Fremont Municipal Water Treatment Plant are located on the Sandusky River. The McDowell Water Treatment Plant of the Bowling Green Municipal Utilities has its intake on the Maumee River. The Maumee watershed is larger than the Sandusky, draining parts of Ohio, Indiana and Michigan. The Sandusky watershed is east of the Maumee's, draining parts of Ohio.

FULL-SCALE STUDIES

When the plants were monitored, samples were collected in timed sequence, based on plug flow. This was done because river water sampling by the WQL (7-9) in their earlier studies and by others for atrazine (10-14) indicated that concentrations changed significantly during runoff events, and suggested that sampling raw and treated waters at or near the same time may misrepresent

treatment effectiveness. No tracer studies were attempted to verify plug flow sampling or describe short circuiting. Errors introduced by deviations from plug flow are not known. Treatment is described in Figures 1, 2, and 3, respectively, for Tiffin, Fremont, and Bowling Green. Samples were collected at the utility's routine collection points to bracket one or more processes or chemical application points. Powdered activated carbon (PAC) is used at the Tiffin and Bowling Green plants for control of periodic taste and odor (T&O). While T&O is not always associated with the springtime runoff, PAC was used during project monitoring in an attempt to determine whether its use at T&O-control doses would be sufficient to lower pesticide concentrations. To evaluate the effectiveness of PAC, plants were sampled with and without PAC application during consecutive runoff events. No attempts were made to optimize processes or chemical application for pesticide control; treatment was routine for the high turbidity and high chlorine demand associated with runoff events. When PAC was applied, doses were within the ranges typically employed for T&O control. Fremont employed an 18 inch cap of Filtrasorb 300 granular activated carbon (GAC) over sand for T&O control. During pesticide sampling, the selected GAC bed had been in place for 30 months.

Water utility personnel collected all samples at plug flow times. Following WQL procedures for sampling river waters (9), no reducing agents or preservatives were added to sample bottles. Routine sampling and analyses for pH, turbidity, and chlorine were performed by utility personnel and followed Standard Methods (15). The utilities forwarded plant operating data and routine water quality data to the DWRD. All three plants were sampled in the Spring of 1984. The Tiffin plant was sampled again in the Spring of 1986.

Monitoring Strategy Previous WQL studies indicated somewhat predictable pesticide occurrence. Following the springtime thaw, tillage, agrichemical application, and planting, the first storm carried both high turbidity and residual pesticides to the Sandusky and Maumee Rivers and their tributaries. Pesticide concentrations were a function of the severity of the storm and the extent to which farmers were able to till and apply agrichemicals between storms. For treatment plant monitoring, attempts were made to begin sampling as river flowrate and turbidity increased, because studies by the WQL and others indicated that pesticide concentrations would increase concurrently. Sampling continued for several consecutive days thereafter, because the same studies indicated that pesticide concentrations would decline gradually (8-14). Assuming significant reductions in pesticide concentrations through processes employing PAC or GAC, the higher concentrations associated with these events were targeted. Because the runoff event and the sampling were typically concluded before the results of the pesticide analyses were known, there was significant trepidation associated with this sampling scheme. Both weather forecasting and the knowledge of the WQL staff of local tillage and planting patterns contributed to the success of the sampling and captured peak pesticide concentrations.

LABORATORY STUDIES

For bench-scale studies at the DWRD, Ohio River (OHR) water was collected at the Cincinnati Water Works, trucked to the DWRD, and stored in stainless steel tanks at room temperature. A submersed centrifugal pump kept sediment in suspension during storage. Groundwater from the Great Miami Aquifer (GMA) in southwest Ohio was collected and stored in a similar

manner. Distilled water was passed through a Milli-Q system employing Filtrasorb 400 (F-400) GAC and stored in glass at room temperature as organic free water (DH_2O). Reagent-grade pesticides were added to distilled water at concentrations approximately 60 percent of solubility, mixed three days, quantitated as stock solutions, and stored at 4°C. Stock solutions were diluted into the appropriate water, mixed 30 minutes, and quantitated as controls.

Single-solute, room temperature, bottle point isotherms utilizing DH_2O, GMA, and OHR waters were conducted for selected pesticides. Prior to spiking with stock solutions, GMA and OHR waters were sand filtered to reduce turbidities to less than 1 ntu. The isotherms employed a 100 x 200 mesh fraction of F-400 that had been pulverized in a ball mill. In these studies, control bottles were sampled over time to assure no degradation or hydrolysis of the pesticide, and carbon-treated bottles were sampled over time to define equilibrium conditions. Isotherm procedures are described in detail elsewhere (16).

Jar tests were employed to simulate coagulation, flocculation, and sedimentation of OHR water. Jar test equipment and procedures described by Hudson were employed (17). Preliminary jar tests of unspiked OHR water defined the coagulant conditions to achieve settled water turbidities below 1 ntu. Stock slurries of technical-grade alum and ferric sulfate were used. To simulate PAC application, PAC stock slurries were dosed following coagulant application during rapid mix. PAC stock slurries were prepared by adding weighed amounts of commercially available WPH or Hydrodarco B (HDB) to DH_2O and mixing until the carbon was thoroughly wetted. These two PACs were chosen because they were applied at Tiffin and Bowling Green, respectively. A third slurry was prepared in a identical manner using the pulverized 200 x 400 mesh fraction of F-400.

Oxidation was simulated in continuously-stirred glass vessels, wherein pesticides were spiked into OHR water, as described, and dosed with stock solutions of chlorine or chlorine dioxide (ClO_2). Chlorine stock was prepared from commerically-available calcium hypochlorite and ClO_2 stock was prepared following Standard Methods (15). Stock and residual concentrations were determined by the DPD titrimetric procedure (15). Sodium thiosulfate was used to halt oxidant reactions.

ANALYTIC METHODS

WQL Procedures Samples taken at water treatment plants were collected in one-quart Mason jars, sealed with Teflon-lined caps, and refrigerated. Jars were prepared at the WQL by detergent washing followed by distilled water rinsing. The WQL staff transported samples from the plants to Heidelberg College where they were refrigerated until extraction. Refrigerated storage time was typically two to 14 days. Studies at the WQL indicated no loss of the pesticides included in this study during refrigerated storage of this duration (18).

Samples were serially extracted with methylene chloride. When river water samples were highly turbid and emulsions occurred, emulsions were broken either by immersing the separatory funnel in an ultrasonic bath or by passing the organic phase through a glass wool column. The extracts were then dried by passing through a sodium sulfate drying column. Concentration occurred in a Kudurna-Danish, Snyder Column apparatus wherein the dried organic phase was transferred to hexane and then isooctane. Concentrates were refrigerated until analysis. Samples were analyzed using capillary, dual-column, gas chromatography with nitrogen-phosphorus thermionic specific detection. Two columns, Durabond-1 and Durabond-5, were

employed. The concentration reported for each pesticide was based on the column providing the optimum percent recovery (based on spiked samples) and precision (based on replicate samples). Quantitation of alachlor, atrazine, cyanazine, linuron, and simazine were provided by the Durabond-5 system. Metolachlor, metribuzin, and carbofuran quantitation were provided by the Durabond-1 system. Details of analytic procedures employed at the WQL have been reported (6).

DWRD Procedures Pesticide analyses of alachlor, metolachlor, atrazine, simazine, carbofuran, linuron, and metribuzin were performed by Environmental Health Research and Testing, Inc. (EHRT) in Cincinnati under contract to the DWRD. Cyanazine was not a contract pesticide.

Stock solutions, controls and treated samples were collected under Teflon seal in glassware of appropriate size by DWRD staff and refrigerated until transported to EHRT. All glassware was distilled water washed and fired at 400°C. Samples were typically extracted the next day upon arrival at EHRT.

Alachlor and metolachlor were serially extracted with hexane or with a 50 percent petroleum ether/hexane mixture. Prior to analysis, concentrates were refrigerated. Following gas chromatography, electron capture detection provided quantitation. Other pesticides were concentrated on a C_{18} column, air dried, solvent extracted, and refrigerated until analysis. They were separated by reverse phase, high performance liquid chromatography, and quantitated by ultraviolet detection. The extraction solvent and elution solvent mixtures were specific for each pesticide. Details of analytic procedures are available from EHRT (19).

Quality Control Procedures Both laboratories calibrated their analytical systems with standards made from materials obtained from the U.S. EPA's Pesticide Repository at Research Triangle Park, North Carolina. The quality control program at the WQL included routine analysis of glassware blanks and field replicates. At both laboratories, periodic analyses of dilution series were used to check linearity and detection limits, and analyses of spikes were performed. The DWRD routinely supplied EHRT with replicates, dilution series, and blanks as blind samples. Because the U.S. EPA performance-evaluation samples for drinking water did not contain the pesticides included in this study, the WQL also conducted an annual interlaboratory sample exchange program. Spiked and unspiked field samples were split at the WQL and sent to water utility, pesticide manufacturer, and private laboratories. In 1984, EHRT participated in the program. EHRT and the WQL results for pesticides analyzed in both laboratories were in good agreement.

RESULTS AND DISCUSSION

Pesticide Trends in Surface Waters A significant number of pesticides were detected during runoff events. Table 3 summarizes pesticides detected in the Maumee River at Bowling Green during the 1984 monitoring. Although all the pesticides cited in Tables 1 and 2 were searched for, only those noted in Table 3 were studied. Others either were not detected, or were found infrequently near detection levels. The frequency of occurrence and concentrations of pesticides that were found were roughly proportional to their use, as given in Tables 1 and 2. The May-to-July period spanned two major runoff events. Concentrations of only two of the cited pesticides had declined to below detection; the other five were still present on the last

sample day in July. The presence of seven pesticides in a water supply is not surprising given their use in Ohio's agricultural areas, and given that pesticide formulations commonly are prepackaged or tank-mixed combinations. For example, the Farm Chemicals Handbook lists atrazine, cyanazine, simazine, metribuzin, linuron, and nine other pesticides as potentially applied in mix with metolachlor (20).

Table 4 similarly summarizes pesticides detected in the Sandusky River at Tiffin for the same period. Typically, pesticides had higher mean and maximum concentrations in the Sandusky River. While both rivers drain watersheds with similar land use, soils, and cropping patterns, the Sandusky watershed is only 20 percent of the size of the Maumee watershed. Previous studies by the WQL have revealed that, as watershed size increases, peak pesticide concentrations decrease, presumably through dilution (9). Such dilution results from the mixing of waters in different stages of hydrographs as tributaries join together. For example, peak atrazine concentrations in 1982 at stations on Honey Creek, the Sandusky River, and the Maumee River, where the drainage areas upstream of the sample stations were 149, 1251, and 6313 sq mi respectively, were 49, 14.5 and 9.5 ug/L, respectively (7). Two small communities use Honey Creek, a Sandusky River tributary, as a source for their public water supplies.

At Fremont, sampling was carried into October to examine the seasonal duration. Table 5 reveals the presence of the highly used pesticides in clarified water for periods of four to six months following their application. Atrazine was still present on the last sample day in October. Wu, et al. (13) found atrazine and alachlor present year round in Maryland surface waters. Both atrazine and its de-ethyl metabolite were detected

year round in Ontario and Quebec surface waters by Frank, et al. (10) and Muir, et al. (14), respectively. When detected year round, winter concentrations were typically below 1 ug/L.

Mean and maximum concentrations at Tiffin and Fremont should not be compared. Lower mean concentrations at Fremont are influenced by declining concentrations in the August-to-October period, and lower maximum concentrations are likely attributable to dilution as Fremont is downstream of Tiffin. Further, for some of the pesticides, pretreatment affects concentration.

There currently exists a paucity of data on the occurrence of several of these pesticides. Atrazine and alachlor have been studied in numerous surface waters (10-14). Both have been studied in midwest groundwaters (21-22). The U.S. EPA has monitored year-round ng/L concentrations of these two pesticides in Mississippi River waters at New Orleans (23); such low concentrations might be expected near the mouth of such a large watershed. Rarely, however, have a family of pesticides, frequently applied in combination, been monitored in the surface waters of the agricultural watersheds where they are applied. The question of how representative these concentrations are will remain unanswered until more monitoring is conducted. Assuming they are representative, the question of their significance also remains. Peaking concentrations during a runoff event may exceed an MCL for a short period of time, but quarterly or annual means may not. The monitoring schedules accompanying MCLs may be critical for pesticide compliance in some surface waters. Further, if MCLs are implemented on the basis of population served, smaller communities on small watersheds with potentially higher pesticide concentrations may not be impacted.

If treatment is to be modified during runoff events in an attempt to control pesticides, increased turbidity may not always serve as a good indicator of pesticide presence. Figure 4 describes turbidity and metolachlor concentration in the Sandusky River at Tiffin during two sampling periods. Three runoff events, represented by three turbidity peaks, were captured. Peak metolachlor concentrations lagged peak turbidity by a few days during each event. The first springtime storm brought with it a turbidity peak near May 20th. Significant concentrations of metolachlor, and other pesticides, accompanied this event. Based on earlier WQL studies (7), however, the metolachlor peaks of June 18 and 25 were more likely a result of further pesticide application in early June, than a result of washing off residual metolachlor from its April/May application. Without additional pesticide application, subsequent storm events typically do not carry increased pesticide concentration along with turbidity (10,11).

In addition to those pesticides cited in Tables 1 and 2, the de-ethyl and de-isopropyl metabolities of atrazine were searched for. They were infrequently detected in both rivers at concentrations below 1 ug/L. Poor and variable recovery, relative to the other pesticides, rendered assessment of their fate during treatment difficult, and they are not reported here.

Control by Conventional Treatment Representative results of sampling three treatment plants for eight pesticides are given in Tables 6, 7 and 8. The results from samples bracketing processes employing PAC or GAC are excluded. Only limited data were presented for linuron in Table 6; it was not detected in the 1984 monitoring. The results indicate that these pesticides pass through clarification, filtration, softening, recarbonation,

and chlorination processes largely unaffected. The small percent removal is attributed to analytic precision at ug/L or ng/L concentrations, or to the inability to truly sample on a plug flow basis. The significant daily changes in pesticide concentration described in Figure 4 suggest the error that can result in sampling across one or more processes of several hours' detention time. Richard, et al. observed similar passing of atrazine through conventional treatment processes when comparing Des Moines tap water to its surface supply (25). Noted exceptions to these compounds passing through conventional treatment processes are the loss of carbofuran at high pH (Table 7), and the chlorination of metribuzin (Table 8). A statistical t-test (24) was applied to the pairs of data representing concentrations before and after the sampled process(es) for the five to nine sample pairs for each runoff event. With the exceptions noted, no sampled process(es) exhibited changes in concentration that were significant at the 95 percent confidence level.

In DWRD jar tests, spiked concentrations of pesticides were unaffected by coagulation and clarification. The data, given in Table 9, are similar to the full-scale data. They indicate that these pesticides are not strongly sorbed to particulates, or complexed with humic materials that are in turn sorbed to particulates, because particulate-control processes provided minimal or no control. This is consistent with the hydrophilic, highly soluble nature of these pesticides. Their inability to complex is further consistent with the relatively low, octanol water coefficents for these pesticides, where these coefficients are known.

Carbofuran. Table 7 indicates that carbofuran failed to survive the softening process wherein the pH was raised. At lower pH values, Tables 7

and 9 suggest insignificant reductions in its concentration. The literature cites carbofuran's instability under alkaline conditions (26), and lists 3-hydroxycarbofuran and carbofuran phenol as hydroxylation and hydrolysis products, respectively (27). Both conversion products are possible under alkaline conditions. No attempts were made in full-scale studies to identify conversion products.

Oxidation. All three full-scale plants practiced breakpoint chlorination. During the runoff events where chlorine demand increased with turbidity, applied chlorine ranged as high as 13 mg/L. In-plant contact times did not exceed 12 hours. With the exception of metribuzin, no significant pesticide/chlorine reactions took place under these conditions. These data are consistent with others. In a study of lower Mississippi River water, neither chlorine nor chlorine dioxide were found to react with atrazine or alachlor at ng/L concentrations. In that study, ozone significantly reduced the concentration of these two pesticides (23). Ozone's reaction with Sandusky and Maumee River pesticides was observed during these studies (28).

When Ohio River water was spiked with pesticides and treated with chlorine or chlorine dioxide, results were similar to the full-scale data. Only metribuzin was found to react with these oxidants, as seen in Tables 10 and 11.

Metribuzin. The reaction of chlorine with metribuzin is demonstrated in Tables 8 and 10. While Table 8 suggests that postchlorination was more effective than prechlorination for apparent control of this herbicide, recall that no reducing agent was added upon sample collection. Therefore,

residual chlorine in clear well samples could have continued to drive the reaction for days until sample extraction.

The DWRD examined this reaction in spiked Ohio River water. Figure 5 illustrates that the reaction can be considered to be first order with respect to metribuzin concentration. The observed rate constant was 3.72 x 10^{-3} min^{-1} and indicates that metribuzin's concentration could be reduced below detection during typical, in-plant detention times. Chromatograms indicated the formation of two other compounds with area counts inversely proportional to metribuzin's in time. Metribuzin is a non-chlorinated, substituted triazine. The presence of additional chromatographic peaks suggests chlorine substitution on the ring or its substituent groups. No attempts were made to identify conversion products. When treated with chlorine dioxide, a similar phenomenon was observed with the formation of one compound having an identical retention time as one of the compounds formed upon chlorination.

Control by Adsorption Results of isotherm studies for the four SDWA pesticides are given in Figure 6 and Table 12. The data indicate that the pesticides are strongly adsorbed. Bauer's isotherm for linuron in a ground water (29) indicates similar capacities to those of atrazine and simazine in GMA water. While the TOC of the filtered ground water (2.6 mg/L) was higher than the TOC of the filtered surface water (2 to 2.5 mg/L), adsorption capacities in GMA water were found to be closer to those in distilled water than to those in OHR water. No synthetic organic compounds (SOCs) were detected in the groundwater, using several procedures (30,31). OHR water, however, has a history of low concentrations of SOCs (32) which could provide a more competitive matrix.

A surface water treatment plant wishing to employ GAC could do so in a deep-bed post-filter mode or in a shallow-bed sand-replacement mode. To predict GAC performance in a sand-replacement bed, the constant pattern homogeneous surface diffusion adsorption model was used (33). Adsorption of alachlor from Ohio River water was selected for modelling as it was poorly adsorbed relative to the other pesticides and would therefore provide a more conservative prediction. Model inputs and predicted use rates for a 3-ft deep, sand-replacement bed are given in Table 13. For adsorption rate data, the model used Dobrzelewski's correlation (35) for the surface diffusion coefficient, and Williamson's correlation (36) for the film transfer coefficient. The validity of these rate correlations for alachlor is not known, and alachlor's presence as a single contaminant may be unlikely. Nevertheless, predicted GAC use rates suggest that control of alachlor, or other studied pesticides, as single contaminants would be less costly than control of T&O by GAC because these use rates are equivalent to bed lives exceeding four years.

No opportunity existed to verify these model predictions. However, alachlor and competing pesticides were detected in Fremont's sand-replacement GAC bed during the 1984 monitoring period. Results are given in Table 14. Fremont's 18-inch deep GAC bed was in place 30 months prior to monitoring, and the pesticide loading onto the bed during previous runoff events is not known. Consequently, comparative GAC use rates could not be determined. Nevertheless, these data suggest that even shallow bed depths can reduce the concentrations of multiple agrichemical pesticides by 50 percent or more for several years. Depending on influent concentrations and MCLs, deep-bed post-filter contactors may not be necessary.

Data compiled for the adsorption of atrazine onto PAC during full-scale treatment are given in Table 15. Using the statistical test of data pairs (24), changes in pesticide concentrations as a result of PAC treatment were significant at the 99 percent confidence level or higher. When atrazine was spiked into Ohio River water and treated with PAC in jar tests, the data in Table 16 were derived. For both full-scale studies and jar tests, relatively high percent removals were observed. The removal was attributed to adsorption onto PAC because, as described in Tables 6 and 9, clarification processes were not effective for control of atrazine. Figure 7 compiles data from Tables 15 and 16 and describes PAC's capacity for atrazine as a function of the atrazine concentration remaining in solution following treatment, that is, these data are treated in a Freundlich relationship. Remaining concentration is very likely different than equilibrium concentration; no attempt was made to fully describe equilibrium capacities for PACs under jar test conditions. The Freundlich fit for these data is good ($r = 0.97$). Good agreement was not expected because the data represent waters having different competitive matrices, different carbon types and different contact times.

Similar relationships were compiled for PAC treatment of other pesticides. They are described in Figure 8 and Table 17. As with atrazine, concentration changes across full-scale processes employing PAC were significant at or above the 99 percent confidence level, and they have relatively good data fits despite the fact that they too are based on varying conditions. All were found to be adsorbable onto the PACs studied.

Comparing the data presented in Figures 6 and 8, significant differences in GAC and PAC adsorption are noted. Adsorption capacities onto PAC

were approximately two orders of magnitude lower than those observed in isotherms. The difference in capacities is most likely due to the limited contact time in PAC jar tests and in sedimentation basins. The fact that coagulants produced an agglomerated mass with the PAC particles that could have altered adsorption kinetics and capacity could help explain the capacity differences. Carbon type was not a cause for the differences because F-400 was used both in the isotherms and in the PAC jar tests.

The capacity for several of the pesticides onto PAC could not be differentiated despite the noted capacity differences in their isotherms. The 95 percent confidence bands about the alachlor data fit are given in Figure 8. Alachlor was chosen because of its central tendency of adsorption capacity among the other pesticides, and because it had a poorer fit ($r = 0.913$) than the others which resulted in a wider band. Alachlor's confidence band encompasses the regression lines for most of the other pesticides. The reason for the similarities in PAC capacities is not known. It seems likely that the agglomerated mass built up around the PAC particles during flocculation had a significant impact.

Using the alachlor regression line given in Figure 8, the PAC requirements to achieve selected effluent concentrations were estimated and are given in Table 18. Given the width of alachlor's confidence band, these estimates may serve for the family of pesticides studied. The data and estimates suggest that PAC applied at T&O-control doses can be sufficient to meet water quality goals when removal requirements do not exceed 80 percent. Depending on influent concentrations and MCLs, PAC may be a better choice than GAC for control of pesticides in surface waters. PAC can be brought on-line only during those times of the year when pesticides are present as runoff.

SUMMARY

The water-soluble pesticides alachlor, atrazine, metolachlor, cyanazine, carbofuran, metribuzin, linuron, and simazine are present in agricultural watersheds in ug/L concentration for periods of two to six months, or longer, following their application. A number of other pesticides known to be used in the same northwestern Ohio watersheds were not detected at ug/L concentrations. Concentrations are generally higher with the first storm following application than with subsequent storms. Turbidity may be a good marker of pesticide presence in the first storm following their application, but residual pesticide concentrations will typically decline thereafter unless additional pesticide is applied. Concentrations generally have higher maximums in smaller watersheds rather than larger ones. Multiple crops and mixed pesticide formulations explain the presence of several pesticides.

Of the pesticides detected, all will move through conventional water treatment plants without control, unless activated carbon is employed. Exceptions are the reaction of metribuzin with chlorine or chlorine dioxide to form what might be chloro-substituted species, and the hydrolysis of carbofuran to other products at softening pH. The relatively high adsorption capacity of these agrichemicals suggest that GAC is cost effective, and in the sand-replacement mode may be sufficient to control seasonal ug/L concentrations. However, PAC applied at T&O-control doses can also be sufficient to reduce these concentrations if moderate percent removal is required to meet an MCL, and can be brought on-line as needed to treat increased pesticide concentrations that accompany storm runoff.

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Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. EPA.

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Table 1

1982 Herbicide Use in Ohio (5)

Herbicide	Percent of Total@
alachlor	26.0
atrazine	20.0
metolachlor	16.7
cyanazine	7.5
butylate	7.0
metribuzin	3.7
linuron	3.0
trifluralin	1.9
EPTC	1.7
simazine	1.2
penoxalin	0.3

@ - by weight

Table 2

1982 Insecticide Use in Ohio (5)

Insecticide	Percent of Total@
carbofuran	20.6
fonofos	25.1
terbufos	25.0
chlorpyrifos	5.6
diazinon	1.9
phorate	1.9
ethoprop	0.1

@ - by weight

Table 3

Maumee River@ Pesticides at Bowling Green, May-July, 1984

Pesticide	Concentration, ug/L Mean #	Maximum	Days Detected*
alachlor	3.58	12.3	20
metolachlor	2.55	7.03	20
atrazine	4.69	8.63	20
cyanazine	1.96	6.12	20
metribuzin	1.25	4.90	16
carbofuran	1.06	2.05	8
simazine	0.29	0.53	20

@ - 6313 sq mi watershed
* - 20 sample days
# - Mean concentration for number of days detected.

Table 4

Sandusky River@ Pesticides at Tiffin, May-July, 1984

Pesticide	Concentration, ug/L Mean #	Maximum	Days Detected*
alachlor	4.89	13.7	19
metolachlor	8.17	22.3	19
atrazine	5.92	11.3	19
cyanazine	1.81	3.63	19
metribuzin	1.82	6.03	18
carbofuran	0.58	1.20	14
simazine	0.44	1.15	19

@ - 1251 sq mi watershed
* - 19 sample days
# - Mean concentration for number of days detected.

Table 5

Pesticides Influent to GAC Filter/Adsorber at Fremont@, May-October, 1984

Pesticide	Concentration, ug/L Mean #	Maximum	Days Detected*	Latest Month Detected
alachlor	3.70	10.5	13	August
metolachlor	6.39	16.3	14	September
atrazine	4.83	9.22	17	October
cyanazine	1.62	4.25	13	August
metribuzin	0.89	3.48	11	July
simazine	0.39	0.77	11	July

@ - Sandusky River, 1251 sq mi watershed
* - 17 sample days
# - Mean concentration for number of days detected.

Table 6

Pesticide Control at Full-Scale Treatment Plants

Process(es)	Alachlor		Metolachlor		Atrazine		Cyanazine	
	Concentration* ug/L	Percent Removal*	Concentration* ug/L	Percent Removal*	Concentration* ug/L	Percent Removal*	Concentration* ug/L	Percent Removal*
C,H,F,H	6.86	24	12.0	17	7.21	14	2.01	20
C,S	3.62	-5	4.64	-3	7.24	-4	2.00	-4
R,H	3.75	3	4.72	2	7.45	3	2.10	0
R,H,F	4.03	15	2.40	11	3.56	9	2.14	2
C,H	9.61	7	17.4	-2	17.8	5	5.50	6
F	8.92	15	17.6	20	16.9	8	5.19	16
H	7.52	-15	14.1	-10	15.5	-7	4.38	-5
H	1.37	1	1.69	3	3.34	6	0.73	2
H	0.94	9	0.98	-27	1.59	-1	0.66	3

Process(es)	Simazine		Linuron	
	Concentration* ug/L	Percent Removal*	Concentration* ug/L	Percent Removal*
C,H,F,H	0.59	10		
C,S	0.34	-10		
R,H	0.37	9		
R,H,F				
C,H	0.78	-1	0.57	-2
F	0.79	21	0.58	19
H	0.62	-6		
H	0.17	7		
H			0.47	4

* - Mean values representing 5 to 9 sample days.
C - Clarification
F - Filtration
S - Softening
R - Recarbonation
H - Chlorination

Table 7

Carbofuran Control at Full-Scale Treatment Plants

Process(es)	Concentration* ug/L	Percent Removal*	pH@
H	0.13	24	7.4
C,H,F,H	0.79	54	7.9
C,S	1.62	100	11.1
S	0.49	100	10.9

* - Mean values representing 5 to 9 sample days.
@ - Highest pH encountered within process(es).
C - Clarification
F - Filtration
S - Softening
H - Chlorination

Table 8

Metribuzin Control at Full-Scale Treatment Plants

Process(es)	Concentration* ug/L	Percent Removal*	Free Chlorine, mg/L	
			Dose*	Residual*
C,S	0.53	0	0	
S	1.34	-21	0	
C,H	4.88	24	6.50	0.97
F	3.70	35		0.44
R,H	0.53	33	2.00	0.34
C,H,F,H†	3.02	85	10.82@	1.90
H†	0.20	60	2.67	0.56
H,R,H†,F	1.23	94	6.63@	1.20
H†	2.41	94	2.95	2.23
H†	0.18	98	3.40	2.49

* - Mean values representing 5 to 9 sampling days.
C - Clarification
S - Softening
F - Filtration
R - Recarbonation
H - Chlorination
† - Postchlorination
@ - Represents pre- and postchlorination.

Table 9

Pesticide Control by Jar Testing@ of Spiked Ohio River Water

Pesticide	Concentration ug/L	Alum# Dose ug/L	Turbidity ntu	Percent Removal
alachlor	43.6	15	42	4
metolachlor	34.3	30	18	11
carbofuran	93.2	30	18	-8
linuron	51.8	30	19	-5
atrazine	65.7	20	7	0
simazine	61.8	20	6	-4
metribuzin	45.4	30	11	-1

@ - raw water pH range = 7.5-8.3, settled water turbidities below 1 ntu
# - technical grade $Al_2(SO_4)_3 \cdot 14\ H_2O$

Table 10

Chlorine Oxidation of Pesticides Spiked into Ohio River Water

Pesticide	Concentration ug/L	Free Chlorine, mg/L Dose	Free Chlorine, mg/L Residual	Time hours	Percent Removal
alachlor	31.0	6.0	4.9	5.83	-5
metolachlor	32.4	4.0	2.7	5.33	2
atrazine	65.8	6.0	1.3	6.25	20
simazine	43.0	3.0	1.2	6	9
linuron	51.8	6.0	1.3	6.25	19
carbofuran	50.0	3.0	1.2	6	-11
metribuzin	60.1	3.1	1.8	6	96

Table 11

Chlorine Dioxide Oxidation of Pesticides Spiked into Ohio River Water

Pesticide	Concentration ug/L	ClO_2, mg/L Dose	ClO_2, mg/L Residual	Time hours	Percent Removal
alachlor	61.0	3.0	1.9	2.5	9
metolachlor	32.4	2.0	1.4	5.33	-4
atrazine	65.8	6.0	3.6	6.25	10
simazine	43.0	1.5	1.0	6	7
linuron	51.8	6.0	3.6	6.25	16
carbofuran	50.0	1.5	1.0	6	-3
metribuzin	34.4	2.0	0.4	2.6	60
metribuzin	60.1	5.9	3.8	6	100

Table 12

Freundlich Isotherm* Coefficients

Pesticide	Water	Freundlich K**	Freundlich 1/n	Concentration Range, ug/L	Number Data Points	Correlation r
atrazine	distilled	283	0.29	4.2-785	16	0.910
	ground@	294	0.36	0.6-317	7	0.989
alachlor	distilled	482	0.26	0.6-512	9	0.991
	ground@	605	0.33	0.2-477	9	0.977
	Ohio River	145	0.38	2.6-46	7	0.881
carbofuran	distilled	275	0.41	2.9-111	10	0.907
	Ohio River	143	0.36	2.2-365	11	0.964
simazine	distilled	151	0.23	0.02-16.5	8	0.939
	ground@	190	0.31	0.2-177	14	0.974

* - Filtrasorb 400, room temperature
** - mg/gram, when equilibrium concentration in mg/L
@ - Great Miami Aquifer

Table 13

Predicted Carbon Use Rates for Alachlor (34)

Influent µg/L	10		20			50		
Effluent µg/L	1	5	1	5	10	1	10	25
Use Rate lb/1000 gal	0.0038	0.0031	0.0061	0.0055	0.0052	0.11	0.01	0.009

Water: filtered Ohio River, pH = 8, temp = 21°C, TOC = 2.5 mg/L
Carbon: Calgon Filtrasorb 400
Contactor: 3 ft depth, 4 gpm/ft^2, 5.62 min EBCT
Rate coefficients: surface diffusion = 0.9-2.46 x 10^{-11} cm^2/sec (35)
film transfer = 2.04 x 10^{-3} cm/sec (36)

Table 14

Pesticide Control by Granular Activated Carbon at Fremont, Ohio, 1984 (34)

SOC	Mean Influent µg/L	Mean Percent Removal[a]	Number Sample Days
alachlor	3.70	72	13
metolachlor	6.39	56	14
atrazine	4.83	47	17
cyanazine	1.62	67	13
simazine	0.39	62	11
metribuzin	0.89	57	11

[a]18-inch, 30-month-old Calgon Filtrasorb 300, EBCT = 2.81 min
loading = 4 gpm/ft^2, treating clarified Sandusky River water

Table 15

Control of Atrazine Using PAC During Full-Scale Treatment

Source Water	Application Point	Concentration[@] ug/L	PAC Type	Percent Removal[@] PAC Dose,[@] mg/L 2.8	3.6	8.4	11	18	33
Sandusky River	clarified	7.83	WPH*	28					
	clarified	2.61	WPH		38				
	raw	12.05	WPH			35			
	raw	4.43	WPH				41		
Maumee River	raw	8.11	HDB#					67	
	raw	2.39	HDB						87

@ - Mean values representing 6 to 9 sample days.
* - Calgon, WPH
# - American Norit, Hydrodarco B

Table 16

Control of Atrazine Using PAC in Ohio River in Jar Tests[@]

Atrazine ug/L	PAC Type	Percent Removal PAC Dose, mg/L 7.5	8.6	14.3	16.7	22.8	33.3	45.6	50	85.7
65.7	HDB#	57							98	
85.4	F400†				64		82			
125	F400†				64		82			
72.4	WPH*		43	60		71		86		95

@ - alum coagulation, pH range 7.5-8.3, 1.5 hr contact time. See Table 9.
† - Calgon, Filtrasorb 400, pulverized to 200 x 400 mesh
# - American Norit, Hydrodarco B
* - Calgon, WPH

Table 17

Pesticide Loading onto PAC

Pesticide	Waters	PACs	K*†	1/n†	Concentration Range, ug/L	Number Data Points	Correlation r
atrazine	S,M,OH	W,H,F	87.8	0.94	0.31-45	17	0.970
simazine	S,M,OH	W,H,F	78.1	0.85	0.03-36.7	22	0.957
alachlor	S,M,OH	W,H,F	85.7	0.88	0.06-36.4	16	0.913
metolachlor	S,M,OH	W,H,F	55.6	0.91	0.98-36.6	7	0.975
carbofuran	S,M,OH	W,H	85.1	0.96	0.19-77.7	13	0.959
metribuzin	S,OH	W	61.7	0.79	0.18-26.6	5	0.999
linuron	S,OH	W,H	98.9	0.79	0.11-37.8	12	0.955

* - mg/gram, when remaining concentration in mg/L
† - As Freundlich coefficients. See Figure 8.
W - Calgon, WPH
H - American Norit, Hydrodarco B
F - Calgon, Filtrasorb 400, pulverized to 200 x 400 mesh
S - Sandusky River water, full-scale treatment, jar test
M - Maumee River water, full-scale treatment
OH - Ohio River water, jar test

Table 18

Powdered Activated Carbon Estimates for Pesticide Control (34)

Influent, µg/L	5	10		20			50		
Effluent, µg/L	1	1	5	1	5	10	1	10	25
Percent Removal	80	90	50	95	75	50	98	80	50
PAC Required, mg/L*	21	46	6	97	18	6	251	26	7

* - Based on treatment data for alachlor. See Table 17.

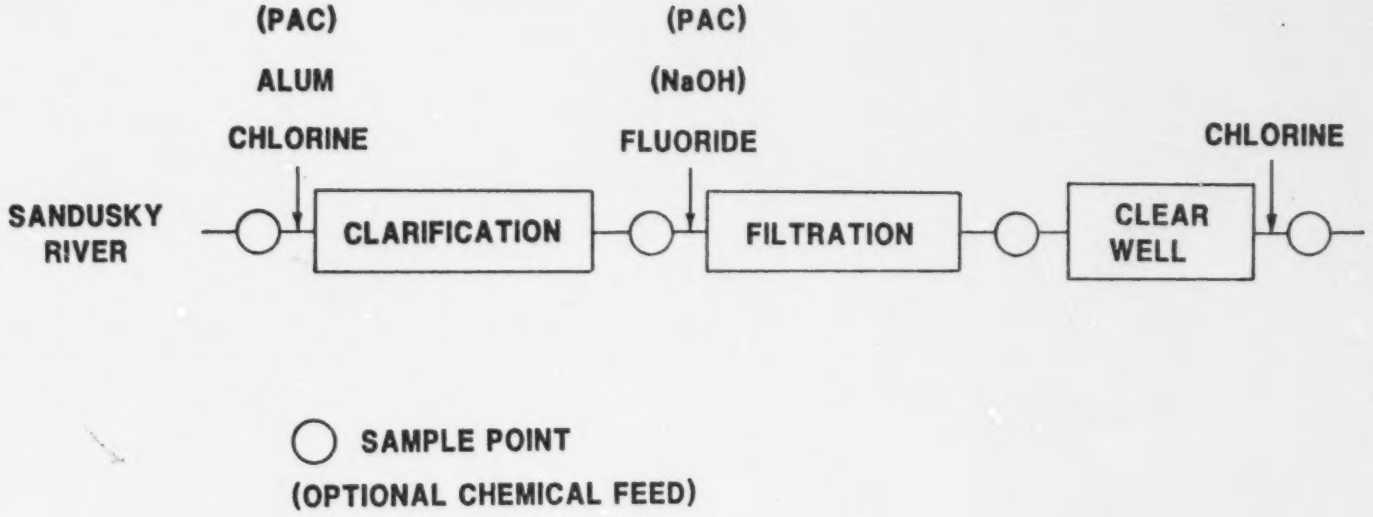

Figure 1. Ohio-American Water Company, Tiffin District

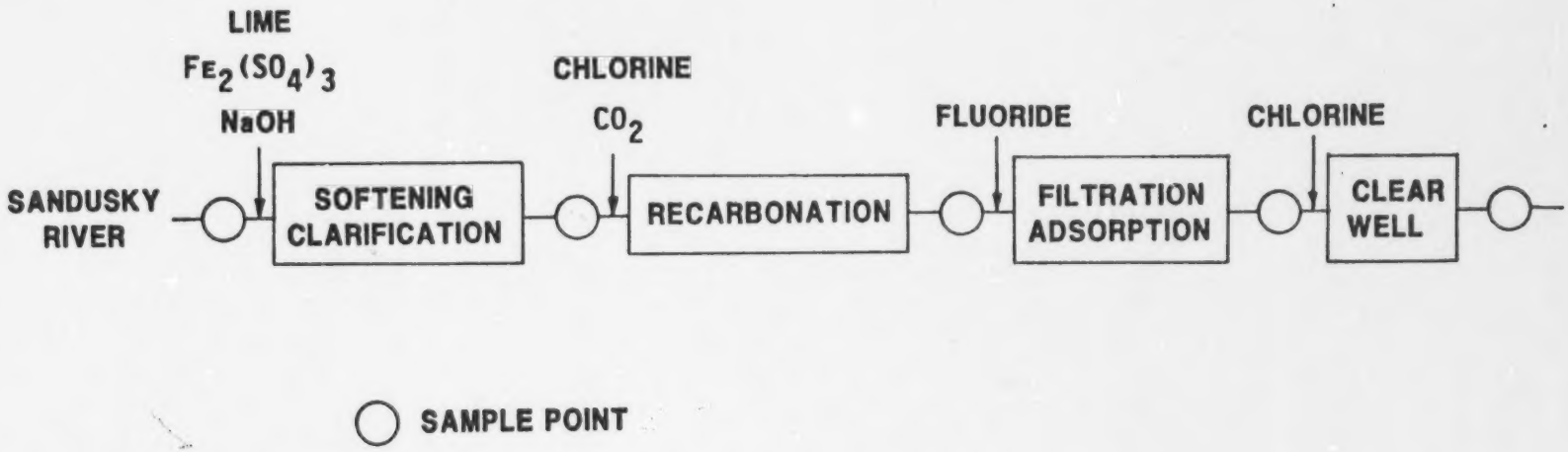

Figure 2. Fremont Municipal Water Treatment Plant, Ohio

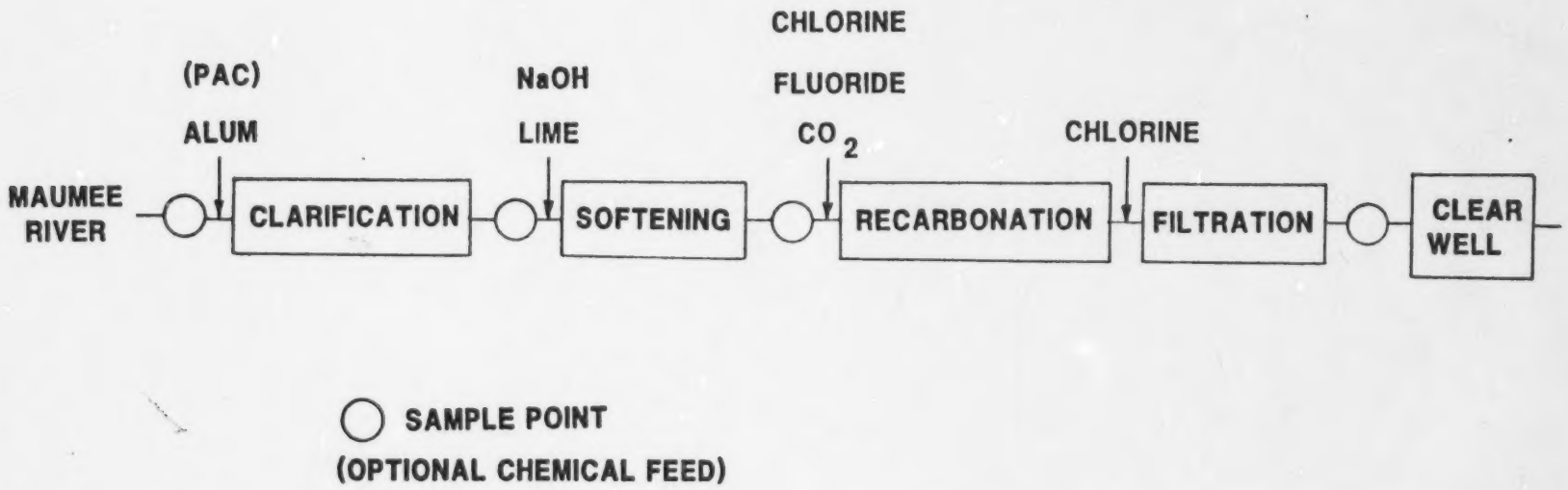

Figure 3. McDowell Water Treatment Plant, Bowling Green, Ohio

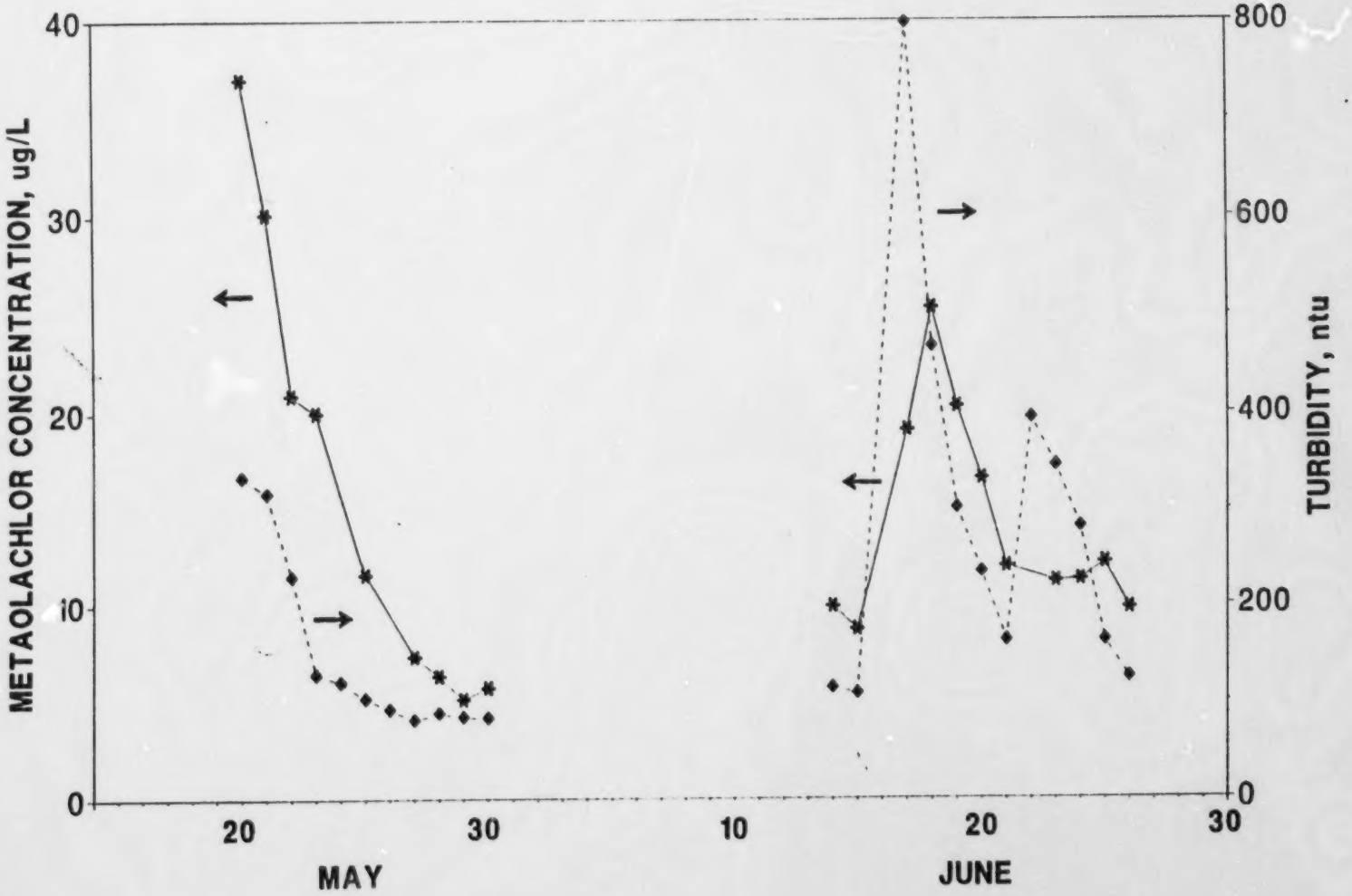

Figure 4. Sandusky River water quality at Tiffin during 1986 storm runnoff events.

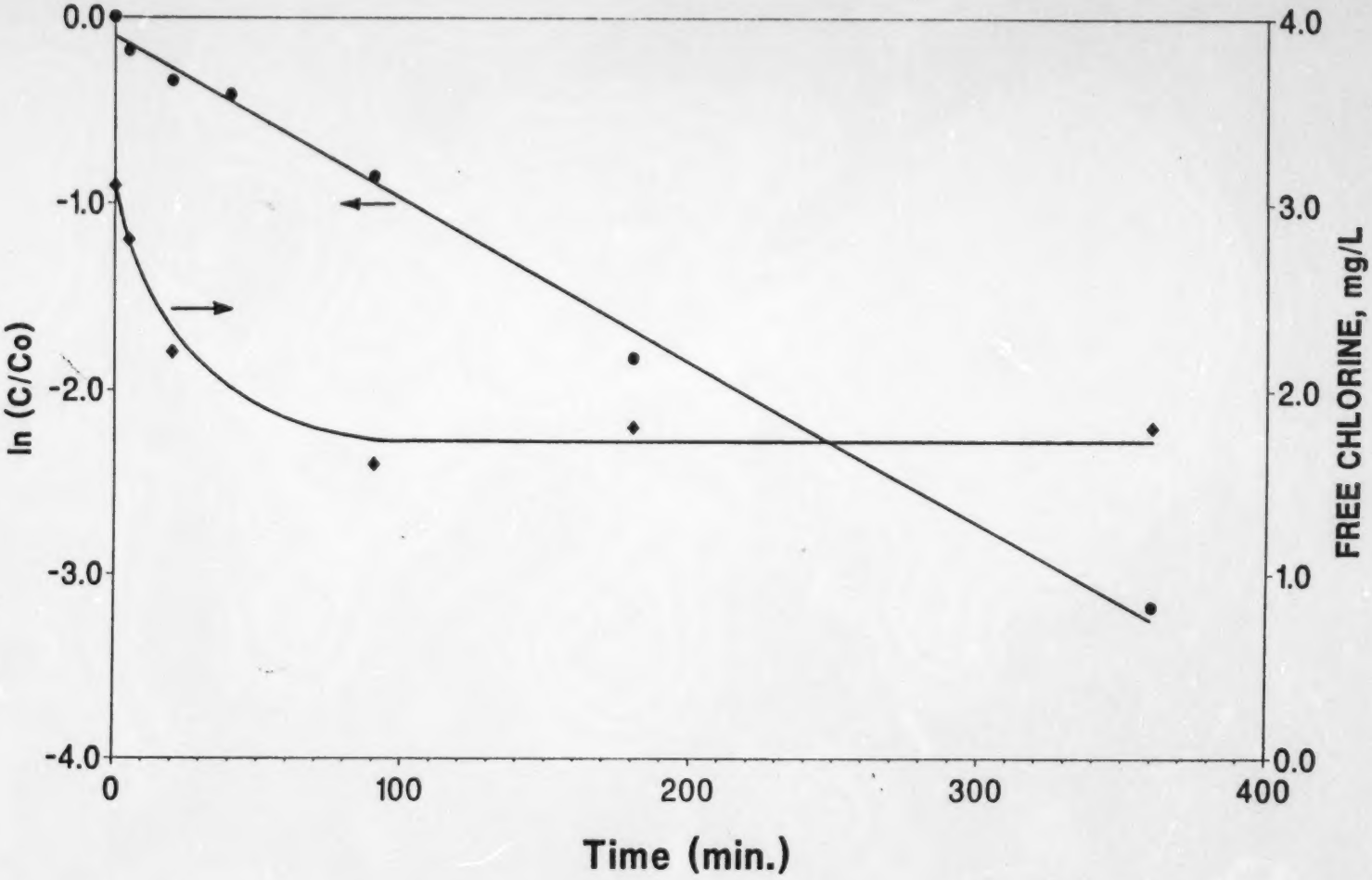

Figure 5. Oxidation of metribuzin in Ohio River water by chlorination.

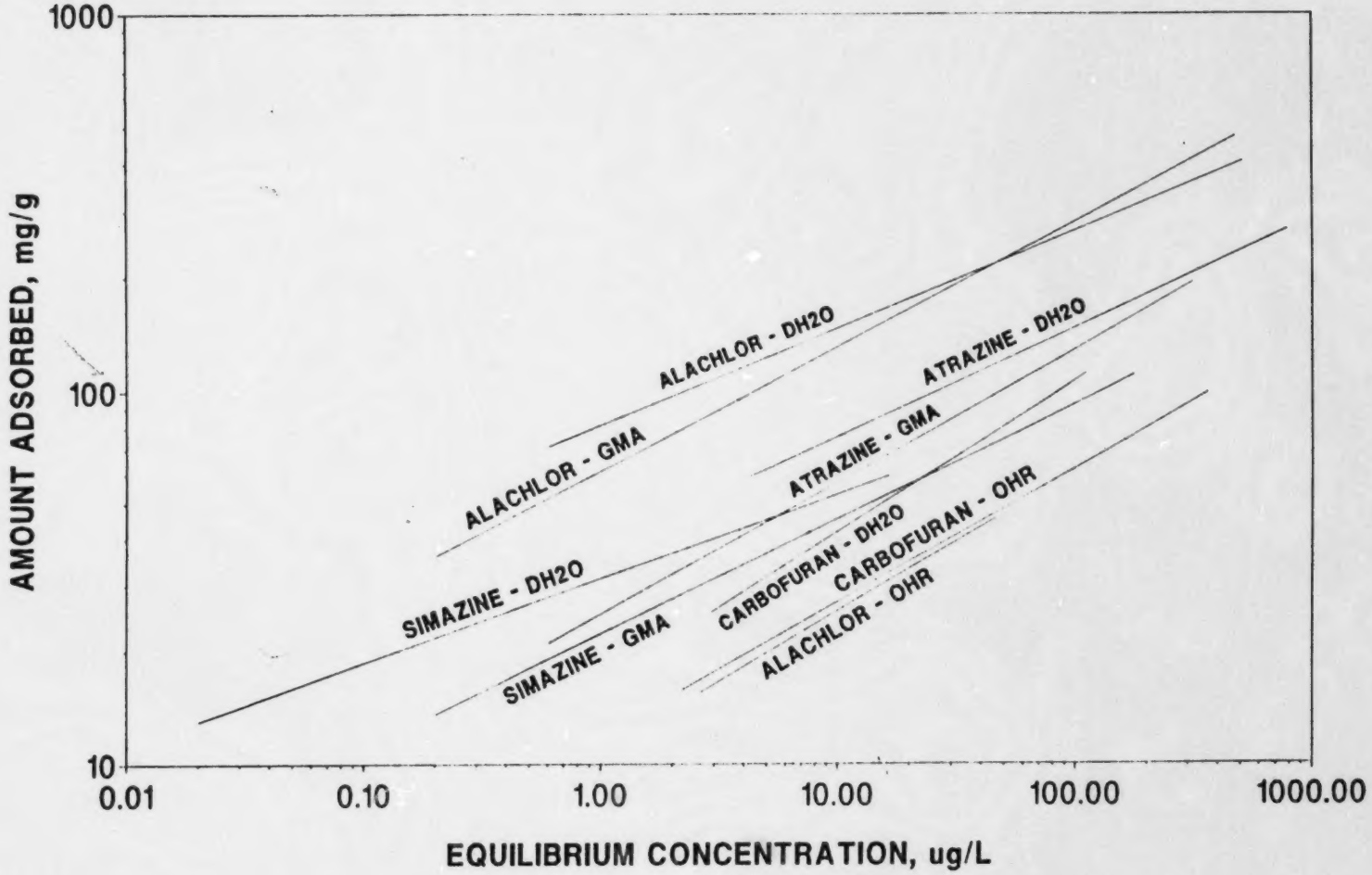

Figure 6. Adsorption isotherms for pesticides (room temperature, Filtrasorb 400).

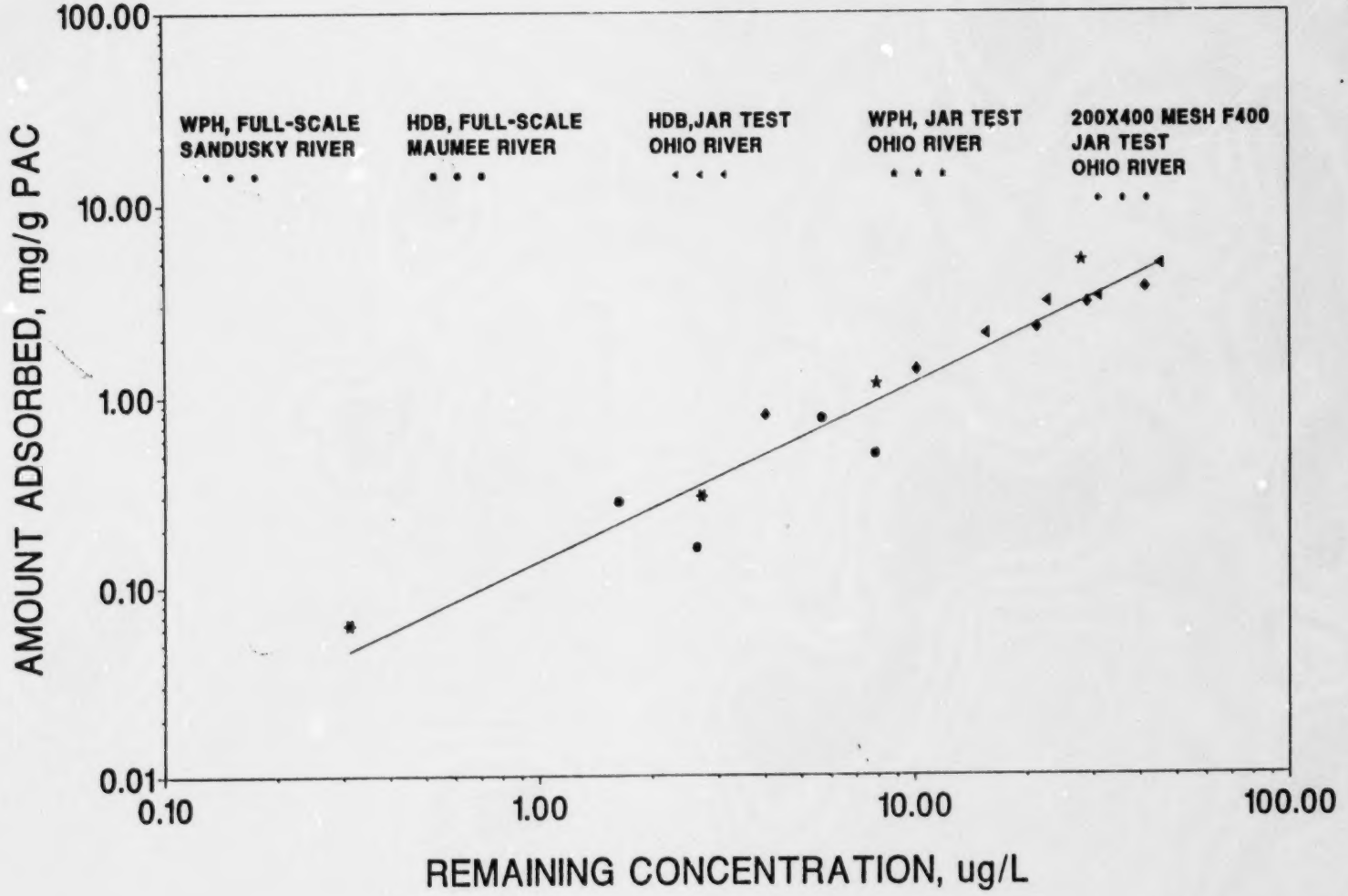

Figure 7. PAC capacity vs. atrazine concentration.

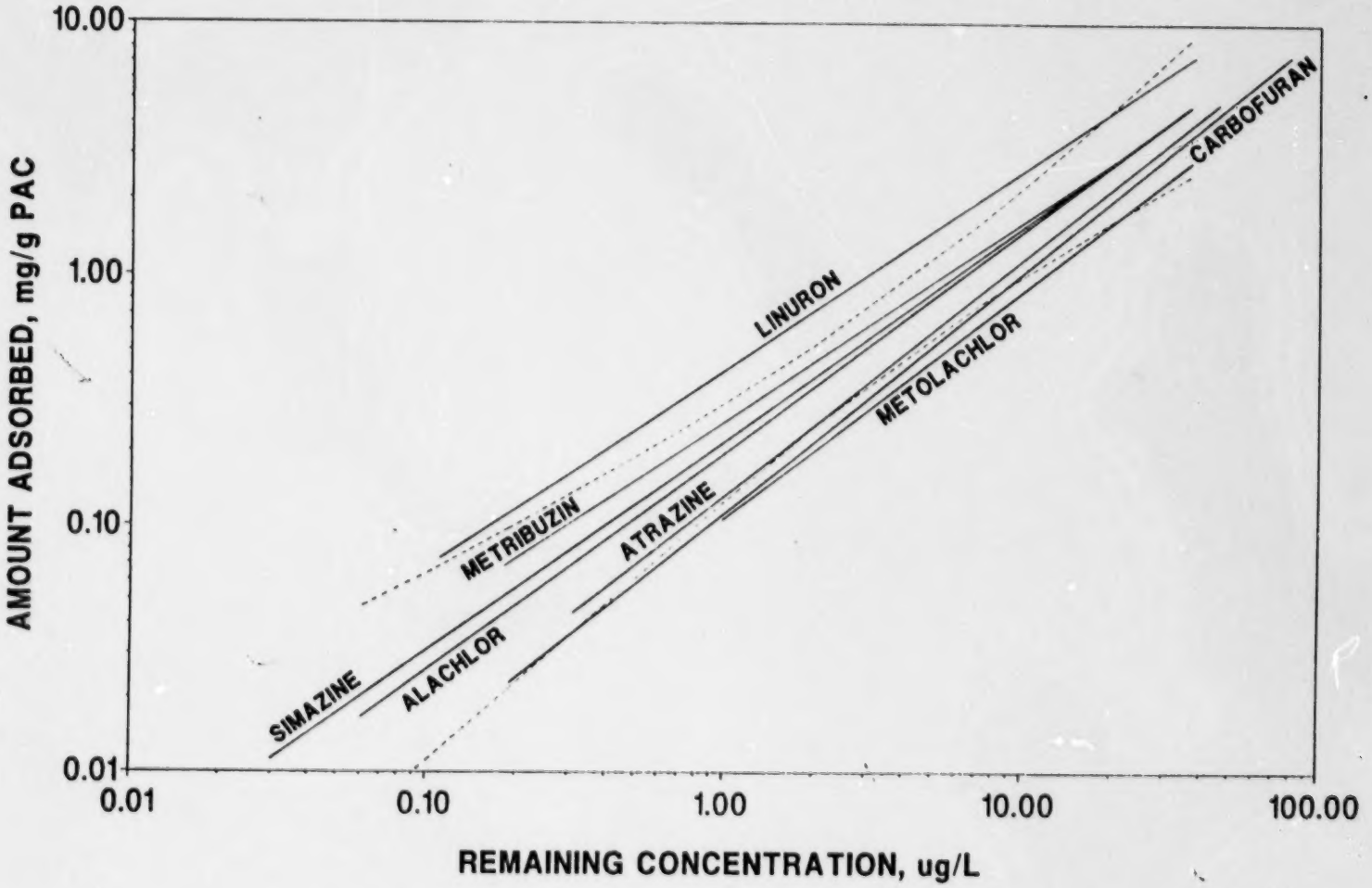

Figure 8. PAC capacity vs. pesticide concentration. (The 95 percent confidence bands for alachlor are given by ---- .)